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(54) Title: DENTIFRICE COMPOSITIONS (57) Abstract <p>Oral compositions, such as oral gels and toothpastes, containing a novel abrasive. An amorphous silica abrasive composition comprising: a) a precipitated silica, said precipitated silica being a low structure precipitated silica having a narrow particle size range distribution of soft particles and having a mean value (MV) particle size ranging from 8 to 14 microns, an oil absorption ranging from 60 to 120 cc/100g, and a mercury intrusion (HGI) void volume of 1.0 to 4.0 cc/g; said precipitated silica, when formulated into a dentifrice, having a Pellicle Cleaning Ratio (PCR) of from 70 to 140 and a Radioactive Dentin Abrasion (RDA) value of from 60 to 130; and wherein the ratio of said PCR to said RDA is at least 1.1; and wherein, as the particle size in microns increases in said silica, the RDA value remains substantially constant; and b) a gel silica comprising particles, preferably having: i) a mean particle size of from 5 to 11 microns (s.d. < 9); ii) an Einlehner hardness of from 3 to 15 for abrasive to brass screen and from 8 to 20 for abrasive to polyester screen; iii) an oil absorption of from 60 ml/100 gm to 130 ml/100 gm; and iv) a radioactive dentin abrasion of from 80 to 200 wherein at least 70 % of all of said particles have a diameter of below 25 microns and wherein the pellicle cleaning ratio is from 90 to 135 and the radioactive dentin abrasion is from 60 to 100 with a pellicle cleaning ratio/radioactive dentin abrasion ratio of from 1.20 to 1.60 and wherein the ratio of precipitated silica to gel silica is from 90:10 to 60:40, respectively.</p>		

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DENTIFRICE COMPOSITIONS

TECHNICAL FIELD

5 The present invention relates to dentifrice compositions such as toothpastes, which provide improved oral cleaning.

BACKGROUND OF THE INVENTION

10 A satisfactory dentifrice composition should have a cosmetic effect upon the teeth, namely, keeping them light colored. It should also clean and remove debris as well, thereby aiding the prevention of tooth decay and promoting gingival health. Abrasives aid in the removal of the tightly adherent pellicle film. This film usually comprises a thin acellular, glycoprotein-mucoprotein coating which adheres to the enamel within minutes after teeth are cleaned. The presence of various food pigments lodged within the film accounts for most instances of teeth discoloration.

15 Ideally, an abrasive should provide satisfactory removal (cleaning) of the pellicle film with minimal damage (abrasion) to oral tissue, i.e. the dentin and enamel.

 Beyond the pellicle cleaning aspect, incorporating an antiplaque agent(s) provides additional benefits. The formation of dental plaque is the primary source of dental caries, gingival and periodontal disease, and tooth loss. Plaque is a mixed

20 matrix of bacteria, epithelial cells, leukocytes, macrophages and other oral exudate. The bacteria associated with plaque can secrete enzymes and endotoxins which can irritate the gums and cause an inflammatory gingivitis. As the gums become increasingly irritated by this process, they have a tendency to bleed, lose their toughness and resiliency, and separate from the teeth. This separation results in

25 periodontal pockets leading in turn to further accumulation of debris, secretions, and more bacteria/toxins. This process eventually leads to destruction of both the hard and soft tissue of the oral cavity.

 The use of a variety of agents to clean the oral cavity and reduce plaque and mouth malodor has been recognized for some time. Examples include: U.S. Patent

30 3,696,191, October 3, 1972 to Weeks; U.S. Patent 3,991,177, November 9, 1976 to Vidra et al.; U.S. Patent 4,058,595, November 15, 1977 to Colodney; U.S. Patent 4,115,546, to Vidra et al.; U.S. Patent 4,138,476, February 6, 1979 to Simonson et al.; U.S. Patent 4,140,758, February 20, 1979 to Vidra et al.; U.S. Patent 4,154,815, May 15, 1979 to Pader; U.S. Patent 4,737,359, April 12, 1988 to Eigen et al.; U.S.

35 Patent 4,986,981, January 22, 1991 to Glace et al.; U.S. Patent 4,992,420, February 12, 1991 to Nesser; U.S. Patent 5,000,939, March 19, 1991 to Dring et al.; Kokai 02/105,898, published April 18, 1990 to Kao Corporation; Kokai 03/128,313, pub-

lished May 31, 1991 to Nippon Kotai Kenkyu and Kokai 03/223,209, published October 2, 1991 to Lion Corporation; U.S. Patent 4,652,444, March 24, 1987 to Maurer; U.S. Patent 4,725,428, February 16, 1988 to Miyahara et al.; U.S. Patent 4,355,022, October 19, 1982 to Rabussay and PCT application WO 86/02831, published May 22, 1986 to Zetachron, Inc.

Abrasives are described in U.S. Patent 4,340,583, July 20, 1982 to Wason, U.S. Patent 3,574,823, April 13, 1971 to Roberts et al., EP Patent 535,943A1, April 7, 1993, McKeown et al., and PCT Patent WO 92/02454, February 20, 1992 to McKeown et al.

Moreover, various combinations of silicas have been described in the art. Silica combinations involving compositions of differing particle sizes and specific surface areas are disclosed in U.S. Patent 3,577,521 to Karlheinz Scheller et al., May 4, 1971 and U.S. Patent 4,618,488 to Maeyama et al., October 21, 1986, respectively. Similarly, U.S. Patents 5,110,574 to Reinhardt et al., May 5, 1992 discloses combining precipitated thickener and polishing silicas to form silica compositions having oil absorption values of at least 200. Further examples of silica combinations include U.S. Patent 5,124,143 to Muhlemann, June 23, 1992 and U.S. Patent 4,632,826 to Ploger et al., December 30, 1986.

While the prior art discloses a variety of silica compositions useful as dental cleaning abrasives, there is still a need for additional compositions providing improved cleaning with minimal abrasion. The present inventor has discovered amorphous silica abrasive compositions comprising precipitated and gel silicas providing improved dental cleaning with minimal abrasion.

Accordingly, it is the object of the present invention to provide a precipitated silica and gel silica compositions providing improved pellicle cleaning without a corresponding increase in dentin or enamel abrasion. Another object of the present invention is to provide an improved method for the prevention or removal tooth stains. A further object of the present invention is to provide an improved method for the prevention or removal of plaque. These and other objects will become readily apparent from the disclosure which follows.

SUMMARY OF THE INVENTION

The present invention relates to amorphous silica abrasive compositions comprising:

- a. a precipitated silica, said precipitated silica being a low structure precipitated silica having a narrow particle size range distribution of soft particles and having a mean value (MV) particle size ranging from 8 to 14 microns, an oil absorption ranging from 60 to 120 cc/100g,

and a mercury intrusion (HGI) void volume of 1.0 to 4.0 cc/g;
said precipitated silica, when formulated into a dentifrice, having a
Pellicle Cleaning Ratio (PCR) of from 70 to 140 and a Radioactive
Dentin Abrasion (RDA) value of from 60 to 130;

and wherein the ratio of said PCR to said RDA is at least 1.1;
and wherein, as the particle size in microns increases in said silica, the
RDA value remains substantially constant; and

b. a gel silica comprising particles
wherein at least about 70% of all of said particles have a diameter of below
about 25 microns and wherein the pellicle cleaning ratio is from about 90 to
about 135 and the radioactive dentin abrasion is from about 60 to about 100
with a pellicle cleaning ratio/radioactive dentin abrasion ratio of from about
1.20 to about 1.60 and wherein the ratio of precipitated silica to gel silica is
from about 90:10 to about 60:40, respectively.

Preferably, the gel silica particles have:

- i.) a mean particle size of from about 5 to about 11 microns (s.d. < 9);
- ii.) an Einlehner hardness of from about 3 to about 15 for abrasive to
brass screen and from about 8 to about 20 for abrasive to polyester
screen;
- iii.) an oil absorption of from about 60 ml/100 gm to about 130 ml/100
gm; and
- iv.) a radioactive dentin abrasion of from about 80 to about 200.

The present invention further relates to dentifrice compositions containing
these abrasives and to a method of cleaning teeth reducing plaque, gingivitis and
calculus using the above compositions.

All percentages and ratios herein are by weight unless otherwise specified.
PCR and RDA are unitless. Additionally, all measurements are made at 25°C unless
otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

By "safe and effective amount," as used herein, means a sufficient amount to
reduce stain and/or plaque/gingivitis without harming the tissues and structures of the
oral cavity.

By the term "orally-acceptable carrier," as used herein, means a suitable vehicle
which can be used to apply the present compositions to the oral cavity in a safe and
effective manner.

The pH of the present herein described compositions range from about 4.0 to
about 9.5, with the preferred pH being from about 6.5 to about 9.0 and the most

preferred pH being 7.0 to about 9.0.

The essential as well as optional components of the compositions of the present invention are described in the following paragraphs.

Abrasive

5 The precipitated silicas of the present invention provide unique Radioactive Dentin Abrasion (RDA) values in the dentifrice compositions of the present invention and are characterized by having a mean value particle size (MV) as measured on a Microtrac Particle Analyzer, in the range of 8 to 14 microns and more preferably from 8-10 microns. The mean value (MV) particle size takes into account skewed
10 particle sizes and speaks to distribution of the particle. Thus, as the mean particle size increases over the range of 8-14 microns as disclosed herein, it would be expected that the RDA would also increase. However, the RDA of these silicas is relatively lower and remains relatively constant or increases at a slower rate. These silicas also have good fluoride compatibility.

15 Certain of these precipitated silicas can also be characterized as agglomerated or cohered silicas wherein subparticles are cohesively bound together during the process of acidulation and/or curing to form the agglomerated precipitated silicas having the mean particle size of 8 to 14 microns. Preferably greater than about 2%, more preferably greater than about 5%, even more preferably greater than about 10%
20 and most preferably greater than about 15% by weight of the precipitated silica particles of the present invention are made up of these agglomerates. Agglomeration is not a result of the addition of a binding agent to the process, but rather is a natural agglomeration caused by physical binding characteristics of the subparticles. It is theorized that during digestion and subsequent curing, the particles of silica become
25 more uniform in size by a process of cohesion of smaller particles and breaking apart of large agglomerates.

 It is therefore theorized that when used in dentifrice formulations, the agglomerated particles break down during the brushing process when in contact with dentin or enamel so that the precipitated silica particles appear to be softer particles
30 when used in the dentifrice formulations. This property, when considered with the fact that the precipitated silicas already possess lower RDA values than prior art silicas, provides dentifrice compositions with increased cleaning but lower abrasiveness. Therefore, a feature of the precipitated silicas of the invention is that they are agglomerated precipitated amorphous silicas of substantially uniform particle
35 size and having mean particles sizes of 8 to 14 microns, and more preferably from 8 to 10 microns, and which have reduced RDA values as compared to the prior art.

A feature of these precipitated silicas is the relationship of the mean particle

size and exhibited RDA. The precipitated silicas of the invention have a mean particle size of 8-14 microns and also unexpectedly have a relatively lower abrasivity or hardness. This relatively lower abrasivity for a low structure silica is unique to the precipitated silicas of the invention.

5 The precipitated silicas of the invention are Low Structure silicas in accordance with the definitions set forth in the J. Soc. Cosmet. Chem. 29., 497-521 (August, 1978), and Pigment Handbook: Volume 1, Properties and Economics, Second Edition, Edited by Peter A. Lewis, John Wiley & Sons, Inc., 1988, p. 139-159. Further, the precipitated silicas may be characterized as having an oil
10 absorption ranging from 60 to 120 cc/100g and preferably 80 to 100 cc/100g, more preferably about 90 cc/100g. The silicas may also be characterized as having a BET surface area in the range of 50 to 250 m²/g.

A further feature of the precipitated amorphous silicas of the invention is the porosity as determined by mercury intrusion (HGI) void volume measurements. The
15 silicas of this invention have mercury intrusion values in the range of 1.0 to 4.0 cc/g and preferably 1.5 to 2.5 cc/g. A further feature of the precipitated silicas of the invention resides in the pH which ranges from 4.0 to 8.5 and preferably from 6.5 to 8.5, as measured in a 5% aqueous slurry.

The Pellicle Cleaning Ratio (PCR) of the inventive silica, which is a
20 measurement of the cleaning characteristics of a dentifrice, ranges from 70 to 140 and preferably from 100 to 130 for the precipitated silica of the invention. The Radioactive Dentin Abrasion (RDA) of the inventive silicas, which is a measurement of the abrasiveness of the precipitated silicas of the invention when incorporated into a dentifrice, ranges from 60 to 130, preferably from 60 to 100, and more preferably
25 from 80 to 90.

The silicas of the invention may also be characterized as having a pour density ranging from 12-16 lb./ft³, a pack density ranging from 25-30 lb./ft³ and median average particle size ranging from 7.0 to 11.0.

These silicas, when incorporated into a dentifrice composition provide an
30 improved PCR/RDA ratio. The PCR/RDA ratio is used to determine the relative ratio of cleaning and abrasion characteristics of a dentifrice formulation. Commercially available dentifrice formulations generally have a PCR/RDA ratio in the range of 0.5 to below 1.0. The precipitated silicas used in the compositions of the present invention provide PCR to RDA ratios to dentifrice formulations of greater
35 than 1, usually in the range of 1.1 to 1.9, but more preferably in the range 1.2 to 1.9.

The precipitated silicas of the invention are preferably characterized as synthetic hydrated amorphous silicas, also known as silicon dioxides or SiO₂. This

definition is intended to include gels and hybrids of silicas such as Geltates.

The RDA (Radioactive Dentin Abrasion) values are determined according to the method set forth by Hefferren, Journal of Dental Research, July-August 1976, pp. 563-573, and described in the Wason U.S. Patent Nos. 4,340,583, 4,420,312 and 5 4,421,527, which publication and patents are incorporated herein by reference.

The PCR (Pellicle Cleaning Ratio) cleaning values are determined by a slightly modified version of the PCR test described in "In Vitro Removal of Stain With Dentifrice", G. K. Stookey, T.A. Burkhard and B. R. Schemerhorn, J. Dental Research, 61, 1236-9, 1982. Cleaning is assessed in vitro by use of the modified 10 pellicle cleaning ratio test. This test is identical to that described by Stookey et al. with the following modifications: (1) a clear artificial pellicle film is applied to bovine chips prior to application of the stained film, (2) solution heating is used rather than radiative heating during film application, (3) the number of brush strokes is reduced to 200 strokes and (4) the slurry concentration is 1 part dentifrice to 3 parts water.

15 In the present specification, oil absorption is measured using the ASTM rub-out method D281. Surface area is determined by the BET nitrogen adsorption method of Brunaur et al., J. Am. Chem. Soc., 60, 309 (1938). To measure brightness, fine powder materials that are pressed into a smooth surfaced pellet are evaluated using a Technidyne Brightimeter S-5/BC. This instrument has a dual beam 20 optical system where the sample is illuminated at a angle of 45°, and the reflected light viewed at 0°. It conforms to TAPPI test methods T452 and T646, and ASTM Standard D985. A series of filters direct to reflected light of desired wavelengths to a photocell where it is converted to an output voltage. This signal is amplified and then processed by an internal microcomputer for display and printout.

25 The average particle size (mean value and median or 50%) is measured using a Microtrac II apparatus, Leeds and Northrup. Specifically, a laser beam is projected through a transparent cell which contains a stream of moving particles suspended in a liquid. Lights rays which strike the particles are scattered through angles which are inversely proportional to their sizes. The photodetector array measures the quantity 30 of light at several predetermined angles. Electrical signals proportional to the measured light flux values are then processed by a microcomputer system to form a multi-channel histogram of the particle size distribution.

The pore volumes (mercury pore volume) are determined using an Autopore II 9220 Porosimeter (Micromeritics Corporation). This instrument measures the void 35 volume and pore size distribution of various materials. Mercury is forced into the voids as a function of pressure and the volume of mercury intruded per gram of sample is calculated at each pressure setting. Total pore volume expressed herein

represents the cumulative volume of mercury intruded at pressures from vacuum to 60,000 psi. Increments in volume (cc/g) at each pressure setting are plotted against the pore radius corresponding to the pressure setting increments. The peak in the intruded volume versus pore radius curve corresponds to the mode in the pore size distribution. It identifies the most common pore size in the sample.

Bulk density is measured by measuring the volume in liters occupied by a given weight of the abrasive and is reported in pounds per cubic foot.

The silicas can be further characterized using a Einlehner At-1000 Abrader to measure the softness of the silicas in the following manner: A Fourdrinier wire screen is weighed and exposed to the action of a 10% aqueous silica suspension for a certain length of time. The amount of abrasion is then determined as milligrams weight lost of the Fourdrinier wire screen per 100,000 revolutions. Brass Einlehner (BE) results are expressed in milligrams.

The silicas preferably possess a BE of less than about 7 and preferably between 2 and 5.

These precipitated silicas are prepared by a fresh water acidulation process wherein silica (silicon dioxide or SiO_2) is precipitated by reaction of an alkali metal silicate and a mineral acid in aqueous solution. The alkali metal silicate may be any alkali metal silicate, but sodium silicate is preferred. While any mineral acid may be used in the process, sulfuric acid is a preferred reactant.

It is a feature of the invention that the process of preparation is a fresh water process, that is, no electrolyte such as alum, Na_2SO_4 , or NaCl , is present during the reaction.

In the preferred process, an aqueous sodium silicate solution is provided wherein the sodium silicate is present in a concentration of about 8.0 to 35 weight percent, preferably 8.0 to 15 weight percent. The $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the silicate solution should range from about 1 to 3.5:1 and preferably from 2.5 to 3.4:1. The sulfuric acid reactant will preferably have a concentration of about 6 to 35% in water, preferably about 9.0 to 15 weight percent.

In the preferred procedure, a small portion of the sodium silicate solution is charged to a reactor for reaction with the sulfuric acid and the remainder of the silicate. In the preferred embodiment, only about 1 to 5% of the total stoichiometric amount of sodium silicate solution, preferably about 2%, should be initially placed in the reactor to serve as initiating nuclei for the silica. This aqueous solution of sodium silicate is then preheated to a temperature in the range of about 80 to 90°C with agitation prior to the addition of the sulfuric acid and remainder of sodium silicate. Agitation may be provided by conventional stirring or agitation equipment.

Thereafter with continued agitation, the remainder of the sodium silicate and sulfuric acid are separately slowly added to the reactor over a limited period of time. In the preferred embodiment, the sodium silicate is metered into the reaction mixture at the rate of about 7 to 12 liters per minute and, more preferably, at the specific rate of 8.94 liters per minute. The sulfuric acid is metered into the reactor at the rate of about 1 to 4 liters per minute but more preferably at the rate of about 2.95 liters per minute.

The sodium silicate solution and sulfuric acid are metered into the sodium silicate solution in the reactor over an addition time of about 40 to 60 minutes, but preferably over a 50 minute addition time. At the end of this addition time at which point the silica has precipitated, the sodium silicate solution addition is stopped but sulfuric acid addition is continued with agitation until a final pH of 5.0 to 5.8 is obtained in the reactor. At this stage, the silica has precipitated to provide a mixture of the precipitated silica and the reaction liquor.

After precipitation of the silica and lowering of the pH of the mixture, the reaction mixture is then subjected to digestion and curing. Digestion is carried out by raising the temperature of the mixture to a temperature of 90° to 98°C, preferably about 95° to 98°C, with continued agitation, over a residence time of about 5 minutes to an hour preferably about 10 to 30 minutes.

Thereafter, the product is cured by further raising the temperature of the mixture to a temperature in the range of about 100°C with continued agitation so as to boil the reaction mixture over a cure time of about one-half hour to about two hours, preferably about 30 minutes to 80 minutes, more preferably about 1 hour. Digestion and curing procedures are critical features of the invention.

On completion of the reaction, the pH is again adjusted to about 5.0, and reaction mixture is filtered and washed with water to remove salts from the filter cake. The filter cake is then dried, preferably by conventional spray drying to produce a precipitated silica containing about 3 to 10% moisture. If necessary, the precipitated silica may be milled to desired particle size by adjusting milling conditions. Because of the uniqueness of the process, milling conditions are easily adjusted to produce silica particles of desired mean values.

Preferred precipitated silica materials include those available from the J.M. Huber Corporation under the tradename, "Zeodent", particularly the silica carrying the designation "Zeodent 128".

Precipitated silica suspensions are prepared in accordance with general methods described, for example, in prior U.S. Patents: 3,893,840, issued July 8, 1975, to Wason; 3,988,162, issued October 26, 1976, to Wason, 4,067,746, issued

January 10, 1978, to Wason; and 4,340,583, issued July 29, 1982, to Wason; all of which are herein incorporated by reference, varying reaction parameters to form precipitated silicas having BE values in the range of from about 1.5 mg to about 6.0 mg and PE values in the range of about 4 mg to about 12 mg, an RDA ranging from about 25 to about 90, and an oil absorption of from about 95ml/100gm to about 135ml/100gm. Reaction parameters which affect the characteristics of the resultant silica include: the rate at which the various reactants are added; the levels of concentration of the various reactants; the reaction pH; the reaction temperature or the rate at which electrolytes are added. The formed suspension is subsequently filtered, followed by a washing and drying of the filtered precipitate. The resulting precipitated silica is next milled to a particle size in which 70% of the particle size distribution is below 20 microns.

In a separate process, gel silicas are prepared in accordance with general methods described, for example, in prior U.S. Patents: 4,153,680, to Seybert, issued May 8, 1979; 4,303,641, to DeWolf II et al., issued December 1, 1981 and 4,632,826, to Ploger et al., issued December 30, 1986, varying reaction parameters to form gel silicas having BE values in the range of from about 3 mg to about 15 mg and PE values in the range of 8 mg to about 20 mg, an RDA ranging from about 80 to about 200, and an oil absorption of from about 130ml/100gm to about 60ml/100gm. Once formed, the gel silica is milled to a particle size in which 70% of the particle size distribution is below 20 microns.

The precipitated and gel silicas, next, are combined (e.g., by physical mixing) to form the amorphous silica compositions of the present invention. The resultant amorphous silica composition can then be incorporated into suitable dentifrice compositions.

In addition to the above described essential components, the dentifrice compositions of the present invention can contain a variety of optional dentifrice ingredients some of which are described below. Optional ingredients include, for example, but are not limited to, adhesives, sudsing agents, flavoring agents, sweetening agents, additional antiplaque agents, abrasives, and coloring agents. These and other optional components are further described in U.S. Patent 5,004,597, April 2, 1991 to Majeti; U.S. Patent 4,885,155, December 5, 1989 to Parran, Jr. et al.; U.S. Patent 3,959,458, May 25, 1976 to Agricola et al. and U.S. Patent 3,937,807, February 10, 1976 to Haefele, all being incorporated herein by reference.

The Pellicle Cleaning Ratio (PCR) of the inventive silica composition, which is a measurement of the cleaning characteristics of a dentifrice, ranges from 90 to 135

and preferably from 100 to 130 for the amorphous silica combination of the invention. The Radioactive Dentin Abrasion (RDA) of the inventive silicas, which is a measurement of the abrasiveness of the precipitated silica combination when incorporated into a dentifrice, ranges from 60 to 10, preferably from 80 to 90.

5 The amorphous silica combinations of the present invention, when incorporated into a dentifrice composition further provide an improved PCR/RDA ratio. The PCR/RDA ratio is used to determine the relative ratio of cleaning and abrasion characteristics of a dentifrice formulation. Commercially available dentifrice formulations generally have a PCR/RDA ratio in the range of 0.5 to below 1.0. The
10 amorphous silicas used in the compositions of the present invention provide PCR to RDA ratios to dentifrice formulations of greater than 1, usually in the range of 1.20 to 1.60, but more preferably in the range 1.25 to 1.50.

The abrasive, in the form of a precipitated silica and gel silica compositions of the present invention, when incorporated into the compositions described herein, is
15 present at a level of from about 6% to about 70%, preferably from about 15% to about 35% when the dentifrice is a toothpaste. Higher levels, as high as 95%, may be used if the composition is a toothpowder.

The abrasive in the compositions described herein is present at a level of from about 6% to about 70%, preferably from about 15% to about 35% when the denti-
20 frice is a toothpaste. Higher levels, as high as 95%, may be used if the composition is a toothpowder.

In addition to the above described essential components, the embodiments of this invention can contain a variety of optional dentifrice ingredients some of which are described below. Optional ingredients include, for example, but are not limited
25 to, adhesives, sudsing agents, flavoring agents, sweetening agents, additional anti-plaque agents, abrasives, and coloring agents. These and other optional components are further described in U.S. Patent No. 5,004,597, April 2, 1991 to Majeti; U.S. Patent No. 4,885,155, December 5, 1989 to Parran, Jr. et al.; U.S. Patent No. 3,959,458, May 25, 1976 to Agricola et al. and U.S. Patent No. 3,937,807, February
30 10, 1976 to Haefele, all being incorporated herein by reference.

PHARMACEUTICALLY ACCEPTABLE CARRIER

The carrier for the components of the present compositions can be any dentifrice vehicle suitable for use in the oral cavity. Such carriers include the usual components of toothpastes, tooth powders, prophylaxis pastes, lozenges, gums and
35 the like and are more fully described hereinafter. Toothpastes are the preferred systems.

Surfactants:

One of the preferred optional agents of the present invention is a surfactant, preferably one selected from the group consisting of sarcosinate surfactants, isethionate surfactants and taurate surfactants. Preferred for use herein are alkali metal or ammonium salts of these surfactants. Most preferred herein are the sodium and potassium salts of the following: lauroyl sarcosinate, myristoyl sarcosinate, palmitoyl sarcosinate, stearoyl sarcosinate and oleoyl sarcosinate.

This surfactant can be present in the compositions of the present invention from about 0.1% to about 2.5%, preferably from about 0.3% to about 2.5% and most preferably from about 0.5% to about 2.0% by weight of the total composition.

Other suitable compatible surfactants can optionally be used along with the sarcosinate surfactant in the compositions of the present invention. Suitable optional surfactants are described more fully in U.S. Patent 3,959,458, May 25, 1976 to Agricola et al.; U.S. Patent 3,937,807, February 10, 1976 to Haeefe; and U.S. Patent 4,051,234, September 27, 1988 to Gieske et al. These patents are incorporated herein by reference.

Preferred anionic surfactants useful herein include the water-soluble salts of alkyl sulfates having from 10 to 18 carbon atoms in the alkyl radical and the water-soluble salts of sulfonated monoglycerides of fatty acids having from 10 to 18 carbon atoms. Sodium lauryl sulfate and sodium coconut monoglyceride sulfonates are examples of anionic surfactants of this type. Mixtures of anionic surfactants can also be utilized.

Preferred cationic surfactants useful in the present invention can be broadly defined as derivatives of aliphatic quaternary ammonium compounds having one long alkyl chain containing from about 8 to 18 carbon atoms such as lauryl trimethylammonium chloride; cetyl pyridinium chloride; cetyl trimethylammonium bromide; di-isobutylphenoxyethyl-dimethylbenzylammonium chloride; coconut alkyltrimethylammonium nitrite; cetyl pyridinium fluoride; etc. Preferred compounds are the quaternary ammonium fluorides described in U.S. Patent 3,535,421, October 20, 1970, to Briner et al., herein incorporated by reference, where said quaternary ammonium fluorides have detergent properties. Certain cationic surfactants can also act as germicides in the compositions disclosed herein. Cationic surfactants such as chlorhexadine, although suitable for use in the current invention, are not preferred due to their capacity to stain the oral cavity's hard tissues. Persons skilled in the art are aware of this possibility and should incorporate cationic surfactants only with this limitation in mind.

Preferred nonionic surfactants that can be used in the compositions of the present invention can be broadly defined as compounds produced by the condensa-

tion of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound which may be aliphatic or alkylaromatic in nature. Examples of suitable nonionic surfactants include the Pluronics, polyethylene oxide condensates of alkyl phenols, products derived from the condensation of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, ethylene oxide condensates of aliphatic alcohols, long chain tertiary amine oxides, long chain tertiary phosphine oxides, long chain dialkyl sulfoxides and mixtures of such materials.

Preferred zwitterionic synthetic surfactants useful in the present invention can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate or phosphonate.

Preferred betaine surfactants are disclosed in U.S. Patent 5,180,577 to Polefka et al., issued January 19, 1993. Typical alkyl dimethyl betaines include decyl betaine or 2-(N-decyl-N,N-dimethylammonio) acetate, coco betaine or 2-(N-coc-N, N-dimethyl ammonio) acetate, myristyl betaine, palmityl betaine, lauryl betaine, cetyl betaine, cetyl betaine, stearyl betaine, etc. The amidobetaines are exemplified by cocoamidoethyl betaine, cocoamidopropyl betaine, lauramidopropyl betaine and the like. The betaines of choice are preferably the cocoamidopropyl betaine and, more preferably, the lauramido propyl betaine.

Chelating agents:

Another preferred optional agent is a chelating agent selected from the group consisting of tartaric acid and pharmaceutically-acceptable salts thereof, citric acid and alkali metal citrates and mixtures thereof. Chelating agents are able to complex calcium found in the cell walls of the bacteria. Chelating agents can also disrupt plaque by removing calcium from the calcium bridges which help hold this biomass intact. However, it is possible to use a chelating agent which has an affinity for calcium that is too high. This results in tooth demineralization and is contrary to the objects and intentions of the present invention.

Sodium and potassium citrate are the preferred alkali metal citrates, with sodium citrate being the most preferred. Also preferred is a citric acid/alkali metal citrate combination. Preferred herein are alkali metal salts of tartaric acid. Most preferred for use herein are disodium tartrate, dipotassium tartrate, sodium potassium tartrate, sodium hydrogen tartrate and potassium hydrogen tartrate. The amounts of chelating agent suitable for use in the present invention are about 0.1% to about 2.5%, preferably from about 0.5% to about 2.5% and more preferably from about

1.0% to about 2.5%. The tartaric acid salt chelating agent can be used alone or in combination with other optional chelating agents.

Other optional chelating agents can be used. Preferably these chelating agents have a calcium binding constant of about 10^1 to 10^5 provide improved cleaning with
5 reduced plaque and calculus formation.

Another group of agents suitable for use as chelating agents in the present invention are the soluble pyrophosphates. The pyrophosphate salts used in the present compositions can be any of the alkali metal pyrophosphate salts. Specific salts include tetra alkali metal pyrophosphate, dialkali metal diacid pyrophosphate,
10 trialkali metal monoacid pyrophosphate and mixtures thereof, wherein the alkali metals are preferably sodium or potassium. The salts are useful in both their hydrated and unhydrated forms. An effective amount of pyrophosphate salt useful in the present composition is generally enough to provide at least 1.0% pyrophosphate ion, preferably from about 1.5% to about 6%, more preferably from about 3.5% to
15 about 6% of such ions. It is to be appreciated that the level of pyrophosphate ions is that capable of being provided to the composition (i.e., the theoretical amount at an appropriate pH) and that pyrophosphate forms other than $P_2O_7^{4-}$ (e.g., $(HP_2O_7)^{3-}$) may be present when a final product pH is established.

The pyrophosphate salts are described in more detail in Kirk & Othmer, Encyclopedia of Chemical Technology, Second Edition, Volume 15, Interscience Publishers (1968), incorporated herein by reference.
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Still another possible group of chelating agents suitable for use in the present invention are the anionic polymeric polycarboxylates. Such materials are well known in the art, being employed in the form of their free acids or partially or preferably
25 fully neutralized water soluble alkali metal (e.g. potassium and preferably sodium) or ammonium salts. Preferred are 1:4 to 4:1 copolymers of maleic anhydride or acid with another polymerizable ethylenically unsaturated monomer, preferably methyl vinyl ether (methoxyethylene) having a molecular weight (M.W.) of about 30,000 to about 1,000,000. These copolymers are available for example as Gantrez AN 139
30 (M.W. 500,000), AN 119 (M.W. 250,000) and preferably S-97 Pharmaceutical Grade (M.W. 70,000), of GAF Chemicals Corporation.

Other operative polymeric polycarboxylates include those such as the 1:1 copolymers of maleic anhydride with ethyl acrylate, hydroxyethyl methacrylate, N-vinyl-2-pyrrolidone, or ethylene, the latter being available for example as Monsanto
35 EMA No. 1103, M.W. 10,000 and EMA Grade 61, and 1:1 copolymers of acrylic acid with methyl or hydroxyethyl methacrylate, methyl or ethyl acrylate, isobutyl vinyl ether or N-vinyl-2-pyrrolidone.

Additional operative polymeric polycarboxylates are disclosed in U.S. Patent 4,138,477, February 6, 1979 to Gaffar and U.S. Patent 4,183,914, January 15, 1980 to Gaffar et al. both patents are incorporated herein by reference, and include copolymers of maleic anhydride with styrene, isobutylene or ethyl vinyl ether, polyacrylic, polyitaconic and polymaleic acids, and sulfoacrylic oligomers of M.W. as low as 1,000 available as Uniroyal ND-2.

Flavoring agents can also be added to dentifrice compositions. Suitable flavoring agents include oil of wintergreen, oil of peppermint, oil of spearmint, oil of sassafras, and oil of clove. Sweetening agents which can be used include aspartame, acesulfame, saccharin, dextrose, levulose and sodium cyclamate. Flavoring and sweetening agents are generally used in dentifrices at levels of from about 0.005% to about 2% by weight.

Dentifrice compositions can also contain emulsifying agents. Suitable emulsifying agents are those which are reasonably stable and foam throughout a wide pH range, including non-soap anionic, nonionic, cationic, zwitterionic and amphoteric organic synthetic detergents. Many of these suitable surfactants are disclosed by Gieske et al, in U.S. Patent No. 4,051,234, September 27, 1977, incorporated herein by reference.

It is common to have an additional water-soluble fluoride compound present in dentifrices and other oral compositions in an amount sufficient to give a fluoride ion concentration in the composition at 25°C, and/or when it is used of from about 0.0025% to about 5.0% by weight, preferably from about 0.005% to about 2.0% by weight, to provide additional anticaries effectiveness. A wide variety of fluoride ion-yielding materials can be employed as sources of soluble fluoride in the present compositions. Examples of suitable fluoride ion-yielding materials are found in U.S. Patent No. 3,535,421, October 20, 1970 to Briner et al. and U.S. Patent No. 3,678,154, July 18, 1972 to Widder et al., both being incorporated herein by reference. Representative fluoride ion sources include: stannous fluoride, sodium fluoride, potassium fluoride, sodium monofluorophosphate and many others. Stannous fluoride and sodium fluoride are particularly preferred, as well as mixtures thereof.

Water is also present in the toothpastes of this invention. Water employed in the preparation of commercially suitable toothpastes should preferably be deionized and free of organic impurities. Water generally comprises from about 10% to 50%, preferably from about 20% to 40%, by weight of the toothpaste compositions herein. These amounts of water include the free water which is added plus that which is introduced with other materials such as with sorbitol.

In preparing toothpastes, it is necessary to add some thickening material to

provide a desirable consistency. Preferred thickening agents are carboxyvinyl polymers, carrageenan, hydroxethyl cellulose and water soluble salts of cellulose ethers such as sodium carboxymethyl cellulose and sodium carboxymethyl hydroxethyl cellulose. Natural gums such as gum karaya, xanthan gum, gum arabic, and gum tragacanth can also be used. Thickening agents in an amount from 0.5% to 5.0% by weight of the total composition can be used.

It is also desirable to include some humectant material in a toothpaste to keep it from hardening. Suitable humectants include glycerin, sorbitol, and other edible polyhydric alcohols at a level of from about 15% to about 70%.

Also desirable for inclusion in the compositions of the present invention are other stannous salts such as stannous pyrophosphate and stannous gluconate and antimicrobials such as quaternary ammonium salts, such as cetyl pyridinium chloride and tetradecylethyl pyridinium chloride, bis-biquanide salts, copper bisglycinate, nonionic anti microbial salts and flavor oils. Such agents are disclosed in U.S. Patent No. 2,946,725, July 26, 1960, to Norris et al. and U.S. Patent No. 4,051,234, September 27, 1977 to Gieske et al., incorporated herein by reference. Other optional components include buffering agents, bicarbonates, peroxides, nitrate salts such as sodium and potassium nitrate. These agents, if present, are included at levels of from about 0.01% to about 30%.

Other useful carriers include biphasic dentifrice formulations such as those disclosed in U.S. Patents 5,213,790, issued May 23, 1993, 5,145,666, issued September 8, 1992, and 5,281,410 issued January 25, 1994 all to Lukacovic et al. and in U. S. Patents 4,849,213 and 4,528,180 to Schaeffer the disclosures of which are incorporated by reference herein.

Suitable lozenge and chewing gum components are disclosed in U.S. Patent No. 4,083,955, April 11, 1978 to Grabenstetter et al., incorporated herein by reference.

The following examples further describe and demonstrate preferred embodiments within the scope of the present invention. The examples are given solely for illustration and are not to be construed as limitations of this invention as many variations are possible without departing from the spirit and scope thereof.

EXAMPLES

The following examples further describe and demonstrate preferred embodiments within the scope of the present invention. The examples are given solely for illustration, and are not to be construed as limitation of this invention as many variations thereof are possible without departing from its spirit and scope.

Example I

A dentifrice composition of the present invention contains the following components as described below.

	Component	Wgt %
	Sorbitol 70% soln	24.200
5	RO Water	24.757
	Glycerin	7.000
	Carboxymethyl Cellulose ¹	0.500
	PEG 6	4.000
	Sodium Fluoride	0.243
10	Sodium Saccharine	0.130
	Monosodium Phosphate	0.415
	Trisodium Phosphate	0.395
	Sodium Tartrate	1.000
	TiO ₂	0.500
15	Silica ²	35.000
	Sodium Lauroyl Sarcosinate (95% active)	1.060
	Flavor	0.800

¹ Supplied by Aqualon Company.

² The amorphous silica ingredient possesses the following characteristics: APS Mean Value = 8.3microns; oil absorption = 108cc/100g; BE = 2.6; PE = 9; PCR = 118; RDA = 80.

The jacket temperature of a mixing tank is set to about 150°F (65°C) to about 160°F (71°C). The humectants and water are added to the mixing tank and agitation is started. When the temperature reaches approximately 120°F (50°C) fluoride, sweetening agents, buffering agents, chelant, coloring agents and titanium dioxide are added. Thickening agents are added to the abrasive and the resulting mixture is added to the mixing tank with high agitation. The surfactant is added to the combination and mixing is continued. The tank is cooled to 120°F (50°C) and the flavoring agents are added. Mixing is continued for approximately 5 minutes.

The resulting composition will have a pH of about 7.

Example II

A dentifrice composition of the present invention contains the following components as described below.

	Component	Wgt %
35	Sorbitol 70% soln	29.810
	RO Water	24.757
	Glycerin	7.000

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	Carboxymethyl Cellulose ¹	0.750
	PEG 6	4.000
	Sodium Fluoride	0.243
	Sodium Saccharine	0.130
5	Monosodium Phosphate	0.415
	Trisodium Phosphate	0.395
	TiO ₂	0.500
	Silica ²	30.000
	Sodium Lauryl Sulfate	1.200
10	Flavor	0.800

¹ Supplied by Aqualon Company.

²The amorphous silica ingredient possesses the following characteristics: APS Mean Value = 8.3 microns; oil absorption = 108cc/100g; BE = 2.6; PE = 9; PCR = 118; RDA = 80.

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Example III

A gum composition of the present invention contains the following components as described below.

	<u>Component</u>	<u>Weight %</u>
	Gum Base	30.000
20	30 parts Estergum	
	45 parts Coumorone Resin	
	15 parts Dry Latex	
	Silica ¹	10.00
	Sugar	40.000
25	Corn Syrup	18.175
	Sodium Lauroyl Sarcosinate	0.075
	Sodium Tartrate	0.250
	Flavor	1.500

¹The amorphous silica ingredient possesses the following characteristics: APS Mean Value = 8.2 microns; oil absorption = 106 cc/100g; BE = 3.3; PE = 10.

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WHAT IS CLAIMED IS:

1. An amorphous silica abrasive composition comprising:
 - a. a precipitated silica, said precipitated silica being a low structure precipitated silica having a narrow particle size range distribution of soft particles and having a mean value (MV) particle size ranging from 8 to 14 microns, an oil absorption ranging from 60 to 120 cc/100g, and a mercury intrusion (HGI) void volume of 1.0 to 4.0 cc/g; said precipitated silica, when formulated into a dentifrice, having a Pellicle Cleaning Ratio (PCR) of from 70 to 140 and a Radioactive Dentin Abrasion (RDA) value of from 60 to 130; and wherein the ratio of said PCR to said RDA is at least 1.1; and wherein, as the particle size in microns increases in said silica, the RDA value remains substantially constant; and
 - b. a gel silica comprising particles, preferably having:
 - i.) a mean particle size of from 5 to 11 microns (s.d. < 9);
 - ii.) an Einlehner hardness of from 3 to 15 for abrasive to brass screen and from 8 to 20 for abrasive to polyester screen;
 - iii.) an oil absorption of from 60 ml/100 gm to 130 ml/100 gm; and
 - iv.) a radioactive dentin abrasion of from 80 to 200wherein at least 70% of all of said particles have a diameter of below 25 microns and wherein the pellicle cleaning ratio is from 90 to 135 and the radioactive dentin abrasion is from 60 to 100 with a pellicle cleaning ratio/radioactive dentin abrasion ratio of from 1.20 to 1.60 and wherein the ratio of precipitated silica to gel silica is from 90:10 to 60:40, respectively.
2. A dentifrice composition according to Claim 1 which further comprises a safe and effective amount of a dentifrice carrier and wherein said abrasive has an RDA, when formulated into a dentifrice formulation, ranging from 60 to 98, a BET surface area ranging from 50 to 250 m²/g, a pH of 5 percent water slurry ranging from 4.0 to 8.5 wherein said silica particles are of substantially uniform particle size with a very narrow distribution within the MV particle size of from 8 to 14 microns, and wherein smaller particles, preferably representing greater than 2%, more preferably greater than 5%, of the precipitated silica, are cohesively adhered to each other by physical binding to be within said MV particle size.

3. A dentifrice composition according to any one of the preceding Claims, wherein said composition further comprising a fluoride ion source wherein the fluoride ion source is selected from the group consisting of sodium fluoride, stannous fluoride, sodium monofluorophosphate, potassium fluoride and mixtures thereof.
4. A dentifrice composition according to any one of the preceding Claims, which further comprises a surfactant selected from the group consisting of sarcosinate surfactants, isethionate surfactants and taurate surfactants.
5. A dentifrice composition according to any one of the preceding Claims, which further comprises from 0.1% to 2.5% of a chelating agent selected from the group consisting of tartaric acid and pharmaceutically-acceptable salts thereof, citric acid and alkali metal citrates and mixtures thereof.
6. A dentifrice composition according to any one of the preceding Claims, wherein said composition has a pH above 7 and wherein the surfactant is selected from the group consisting of sodium lauroyl sarcosinate, sodium decyl sarcosinate, sodium myristyl sarcosinate, sodium stearyl sarcosinate, sodium palmitoyl sarcosinate, sodium oleoyl sarcosinate and mixtures thereof.
7. A dentifrice composition according to any one of the preceding Claims, further comprising from 15% to 70% of a humectant selected from among the group consisting of glycerin, sorbitol, Propylene glycol and mixtures thereof.
8. A dentifrice composition according to any one of the preceding Claims, wherein the surfactant is a combination of sodium lauroyl sarcosinate and cocoamidopropyl betaine and the chelating agent is a combination of tartaric acid and sodium tartrate.
9. A dentifrice composition according to any one of the preceding Claims, in the form of a toothpaste, tooth powder, prophylaxis paste, lozenge, gum, or oral gel.

10. A process of manufacturing a dentifrice composition comprising the steps of:
- a. precipitating a silica, wherein said silica is precipitated by the following steps:
 - i) providing an aqueous solution of sodium silicate having a concentration of 8.0 to 35 weight percent, and an $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of 1 to 3.5:1;
 - ii) providing a sulfuric acid aqueous solution having a concentration of 6 to 35 percent;
 - iii) charging to a reactor 1 to 5 percent of the stoichiometric amount of said sodium silicate solution with agitation;
 - iv) heating said solution of said sodium silicate to a temperature in the range of 80 to 90°C;
 - v) slowly adding to said reactor, sulfuric acid and the remainder of said sodium silicate solution, said addition being conducted over a period of time wherein the sodium silicate is metered into the reaction mixture at the rate of 7 to 12 liters per minute and the sulfuric acid is metered into the reactor at the rate of 1 to 4 liters per minute;
 - vi) continuing the addition of sodium silicate and sulfuric acid to said reactor over an addition time of 40 to 60 minutes;
 - vii) stopping the sodium silicate solution addition but continuing the sulfuric acid solution addition with agitation until a final pH of 5.0 to 5.8 is obtained in the reactor to provide a precipitated silica in the reaction liquor;
 - viii) raising the temperature of said reaction mixture to a temperature of 90° to 98°C for a time of 10 minutes to 1 hour while continuing agitation; and
 - ix) curing the reaction mixture by boiling said mixture for a period of at least 30 minutes to two hours to cause formation of substantially uniform particle size precipitated silica;
 - x) cooling the reaction mixture and recovering the precipitated silica; and
 - b. combining the precipitated silica of step a. with from 0.1% to 99% of an orally-acceptable dentifrice carrier.

INTERNATIONAL SEARCH REPORT

Ir. onal Application No
PCT/US 96/05496

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/16 C01B33/193

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K C09C C09K C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 02454 (JOSEPH CROSFIELD & SONS LIMITED) 20 February 1992 see the whole document ---	1-10
A	WO,A,90 05113 (J.M. HUBER CORPORATION) 17 May 1990 see the whole document ---	1-10
A	EP,A,0 236 070 (UNILEVER PLC) 9 September 1987 see the whole document ---	1-10
A	EP,A,0 535 943 (JOSEPH CROSFIELD & SONS LTD.) 7 April 1993 see the whole document ---	1-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

2 August 1996

Date of mailing of the international search report

13. 08. 96

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INTERNATIONAL SEARCH REPORT

In International Application No
PCT/US 96/05496

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	DE,A,35 27 280 (LION CORPORATION) 6 February 1986 cited in the application see table 1 ---	1
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 96/05496

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-9
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The physical characteristics "pellicle cleaning ratio (PCR)" and "Einlehner hardness" are unusual parameters in the field of cosmetics. The search was limited to the general inventive idea, the examples and searchable parameters.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No
PCT/US 96/05496

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/05496

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